

We claim:

1. An ordered biopolymeric material, comprising a rod-shaped polypeptide that comprises a self-fabricating helical sequence and a metal-binding group at the N-terminus or C-terminus or both; and a metal; wherein the metal coordinates to an N-terminal or C-terminal functional group; and wherein the rod-shaped polypeptide is a component of a layer, wherein the axis of the rod-shaped polypeptide is perpendicular to the plane of the layer.

2. The ordered biopolymeric material of claim 1, wherein the self-fabricating helical sequence of said rod-shaped polypeptide is selected from the group consisting of a silk helical sequence, a collagen helical sequence, a keratin helical sequence, an actin helical sequence, and a chorion helical sequence.

3. The ordered biopolymeric material of claim 1, wherein the self-fabricating helical sequence of said rod-shaped polypeptide is a silk helical sequence.

4. The ordered biopolymeric material of claim 1, wherein the self-fabricating helical sequence of said rod-shaped polypeptide comprises alanine, glycine, proline, or serine.

5. The ordered biopolymeric material of claim 1, wherein said metal-binding group at the N-terminus or C-terminus or both is selected from the group consisting of glutamic acid, lysine, histidine, cysteine, and asparagine.

6. The ordered biopolymeric material of claim 1, wherein the metal is a rare-earth metal.

7. The ordered biopolymeric material of claim 1, wherein the metal is Gd, Dy, Pr, Ce, Er, Ho, or a mixture thereof.

8. The ordered biopolymeric material of claim 1, wherein the metal is Gd, Dy, or a mixture thereof.

25 9. The ordered biopolymeric material of claim 1, further comprising a second metal.

10. The ordered biopolymeric material of claim 9, wherein the second metal is a transition metal selected from the group consisting of Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, La, Hf, Ta, W, Re, Os, Ir, Pt, Au, and Hg.

11. The ordered biopolymeric material of claim 9, wherein the second metal is a second row transition metal selected from the group consisting of Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, and Cd.

12. The ordered biopolymeric material of claim 9, wherein the second metal is a third row transition metal selected from the group consisting of La, Hf, Ta, W, Re, Os, Ir, Pt, Au, and Hg.

13. The ordered biopolymeric material of claim 9, wherein the second metal is selected
5 from the group consisting of Cr, Mo, Co, Ni, Cu, Au, Fe, Hg, Ta, W, Pt, Ag, Pd, and mixtures thereof.

14. The ordered biopolymeric material of claim 1, further comprising a metalloid selected from the group consisting of B, Si, Ge, As, Sb, Te, and Po.

15. The ordered biopolymeric material of claim 14, wherein the metalloid is Si, Ge or a
10 mixture thereof.

16. The ordered biopolymeric material of claim 1, wherein the rod-shaped polypeptide that comprises a self-fabricating helical sequence and a functional group at the N-terminus or C-terminus or both is selected from the group consisting of:

E₃(GAGAGS)₄E₃,

15 E₅(GAGAGS)₄E₅,

E₆(GAGAGS)₄E₆,

E₃(GSPGPP)₆E₃,

E₅(GSPGPP)₆E₅,

E₆(GSPGPP)₆E₆,

20 E₂(GAGAGS)₍₁₋₆₎E₄,

E₄(GAGAGS)₍₁₋₆₎E₂,

EEEAAAKEEE,

EECCAKEECE,

EEEGAGAGSEEE,

25 NNECACKCCNE,

EAAKEAAAK,

CCEAAAKDAAHC,

HCAAEEAAAKCH,

NGCGN(GPAGPP)₂NGCGN,

30 NGCGN(GAGAGA)NGCGN,

C(N)₃(GGAGVA)₆(N)₃C,

N₂(GAGAGA)(GPCGPP)(GAGAGA)N₂,

NGCGN(GSHGGS)(GAGAGA)N₅,

- N₂ H (GCAGAA)(GAAGAG) N₂,
N₂ GCPGPP (GAAGPGAAG)GPPGPH(N)₃,
N₅ GPCGHP GCPGPH (GPAGPP) (N)₅,
NGCGN(helical sequence)NGCGN,
5 NGCGN(helical sequence)H(helical sequence) N₅,
L₄ H GC(helical sequence)L₅,
(GL)₅ GC(helical sequence)H(GL)₅, and
(LV)₅ GPCGHP GCPGPH (helical sequence)(LV)₅.
17. The ordered biopolymeric material of claim 1, wherein the thickness of the layer is
10 less than or equal to about 10 nm.
18. The ordered biopolymeric material of claim 1, wherein the thickness of the layer is
less than or equal to about 5 nm.
19. The ordered biopolymeric material of claim 1, wherein the thickness of the layer is
less than or equal to about 1 nm.
- 15 20. A method of preparing the ordered biopolymeric material of claim 1, comprising:
a) preparing an aqueous solution comprising a lyophilized oligopeptide, wherein
the oligopeptide comprises a self-fabricating helical sequence and a metal-binding group;
b) adding a metal to the aqueous solution of step a);
c) optionally agitating the mixture from step b);
d) optionally heating the mixture from step b) or c) at elevated temperatures;
e) allowing the mixture from step b), c) or d) to stand for about 1 hour to about 24
20 hours;
f) separating any suspended metal from the mixture of step e); and
g) allowing the resulting solution from step f) to dry.
- 25 21. The method of claim 20, wherein the self-fabricating helical sequence is selected
from the group consisting of a silk helical sequence, a collagen helical sequence, a keratin
helical sequence an actin helical sequence, and a chorion helical sequence.
22. The method of claim 20, wherein the self-fabricating helical sequence is a silk
helical sequence.
- 30 23. The method of claim 20, wherein the self-fabricating helical sequence comprises
alanine, glycine, proline, or serine.
24. The method of claim 20, wherein the self-fabricating helical sequence is selected
from the group consisting of:

- E₃(GAGAGS)₄E₃,
E₅(GAGAGS)₄E₅,
E₆(GAGAGS)₄E₆,
E₃(GSPGPP)₆E₃,
5 E₅(GSPGPP)₆E₅,
E₆(GSPGPP)₆E₆,
E₂(GAGAGS)₍₁₋₆₎E₄,
E₄(GAGAGS)₍₁₋₆₎E₂,
EEEAAAKEEE,
10 EECCAKEECE,
EEEGAGAGSEEE,
NNECACKCCNE,
EAAKEAAAK,
CCEAAAKDAAHC,
15 HCAAEAAAKCH,
NGCGN(GPAGPP)₂NGCGN,
NGCGN(GAGAGA)NGCGN,
C(N)₃(GGAGVA)₆(N)₃C,
N₂(GAGAGA)(GPCGPP)(GAGAGA)N₂,
20 NGCGN(GSHGGS)(GAGAGA)N₅,
N₂H(GCAGAA)(GAAGAG)N₂,
N₂ GCPGPP (GAAGPGAAG)GPPGPH(N)₃,
N₅ GPCGHP GCPGPH (GPAGPP)(N)₅,
NGCGN(helical sequence)NGCGN,
25 NGCGN(helical sequence)H(helical sequence)N₅,
L₄H GC(helical sequence)L₅,
(GL)₅ GC(helical sequence)H(GL)₅, and
(LV)₅ GPCGHP GCPGPH (helical sequence)(LV)₅.
25. The method of claim 20, wherein the metal-binding group is selected from the group
30 consisting of glutamic acid, lysine, histidine, cysteine, and asparagine.
26. The method of claim 20, wherein the metal is a powdered rare-earth metal oxide.
27. The method of claim 20, wherein the metal is a rare-earth metal chloride.

28. The method of claim 27, wherein the rare-earth metal chloride is dissolved in dilute HCl.

29. The method of claim 20, wherein the metal is Gd, Dy, Pr, Ce, Er, Ho, or a mixture thereof.

5 30. The method of claim 20, wherein the metal is Gd, Dy, or a mixture thereof.

31. A method of preparing a structured peptide-metal-complexed material comprising:
a) combining a peptide that is amphiphilic or rigid or both that contains a metal-binding group with a metal to give a mixture;

10 b) removing a portion of the solvent from the mixture to generate a liquid crystalline material;

c) adjusting the temperature of the liquid crystalline material; and
d) removing a portion of solvent from the liquid crystalline material.

32. The method of claim 31, wherein peptide comprises a sequence selected from the group consisting of :

15 E₃(GAGAGS)₄E₃,

E₅(GAGAGS)₄E₅,

E₆(GAGAGS)₄E₆,

E₃(GSPGPP)₆E₃,

E₅(GSPGPP)₆E₅,

20 E₆(GSPGPP)₆E₆,

E₂(GAGAGS)₍₁₋₆₎E₄,

E₄(GAGAGS)₍₁₋₆₎E₂,

EEEAAAKEEE,

EECCAKEECE,

25 EEEGAGAGSEEE,

NNECACKCCNE,

EAAKEAAAK,

CCEAAAKDAAHC,

HCAAEAAAKCH,

30 NGCGN(GPAGPP)₂NGCGN,

NGCGN(GAGAGA)NGCGN,

C(N)₃(GGAGVA)₆(N)₃C,

N₂(GAGAGA)(GPCGPP)(GAGAGA)N₂,

NGCGN(GSHGGS)(GAGAGA) N₅,
N₂ H (GCAGAA)(GAAGAG) N₂,
N₂ GCPGPP (GAAGPGAAG)GPPGPH(N)₃,
N₅ GPCGHP GCPGPH (GPAGPP) (N)₅,
5 NGCGN(helical sequence)NGCGN,
NGCGN(helical sequence)H(helical sequence) N₅,
L₄ H GC(helical sequence)L₅,
(GL)₅ GC(helical sequence)H(GL)₅, and
(LV)₅ GPCGHP GCPGPH (helical sequence)(LV)₅.

- 10 33. The method of claim 31, wherein the metal is a rare-earth metal.
34. The method of claim 31, wherein the metal is Gd, Dy, Pr, Cs, Er, Ho, or a mixture thereof.
35. The method of claim 31, wherein the metal is Gd, Dy, or a mixture thereof.
36. The method of claim 31, wherein the metal is a transition metal selected from the
15 group consisting of Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd,
Ag, Cd, La, Hf, Ta, W, Re, Os, Ir, Pt, Au, and Hg.
37. The method of claim 31, wherein the metal is a first row transition metal selected
from the group consisting of Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn.
38. The method of claim 31, wherein the metal is a second row transition metal selected
20 from the group consisting of Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, and Cd.
39. The method of claim 31, wherein the metal is a third row transition metal selected
from the group consisting of La, Hf, Ta, W, Re, Os, Ir, Pt, Au, and Hg.
40. The method of claim 31, wherein the metal is a transition metal selected from the
group consisting of Cr, Mo, Co, Ni, Cu, Au, Fe, Hg, Ta, W, Pt, Ag, Pd, and mixtures
25 thereof.
41. The method of claim 31, wherein the metal is a transition metal in the form of a
complex selected from the group consisting of: anionic polyoxometallates, polynuclear
cationic species, and chiral complexes.
42. The method of claim 41, wherein the anionic polyoxometallates are selected from
30 the group consisting of: isopolymolybdates, heteropolymolybdates, isopolytungstates, and
heteropolytungstates; the polynuclear cationic species are selected from the group
consisting of Ta₆Cl₁₂²⁺, Ta₆Br₁₂²⁺, W₆Cl₈⁴⁺, and W₆Br₈⁴⁺; and the chiral complexes are

selected from the group consisting of tris-bipyridylruthenium(II) and tris(tetramminedihydroxocobalt(III))cobalt(III) cation.

43. An ordered biopolymeric material, comprising a rod-shaped polypeptide that comprises a self-fabricating helical sequence, wherein the self-fabricating helical sequence is selected from the group consisting of:

EEEA~~AA~~AKEEE,
EECCA~~KEE~~ECE,
EEEGAGAGSEEE,
NNECACKCCNE,
EAAKEAAAK,
CCEAAAKDAAHC, and
HCAAEEAAKCH;

and wherein the rod-shaped polypeptide is a component of a layer, wherein the axis of the rod-shaped polypeptide is perpendicular to the plane of the layer.

15 44. A peptide sequence selected from the group consisting of:

EEEA~~AA~~AKEEE,
EECCA~~KEE~~ECE,
EEEGAGAGSEEE,
NNECACKCCNE,
EAAKEAAAK,
CCEAAAKDAAHC, and
HCAAEEAAKCH.

45. A polymer comprising the peptide sequence of claim 44.

46. A rod-shaped polypeptide that comprises a self-fabricating helical sequence and a metal-binding group at the N-terminus or C-terminus or both, wherein the self-fabricating helical sequence is selected from the group consisting of:

E₃(GAGAGS)₄E₃,
E₅(GAGAGS)₄E₅,
E₆(GAGAGS)₄E₆,
E₃(GSPGPP)₆E₃,
E₅(GSPGPP)₆E₅,
E₆(GSPGPP)₆E₆,
E₂(GAGAGS)₍₁₋₆₎E₄,

- E₄(GAGAGS)₍₁₋₆₎E₂,
EEEAAAKEEE,
EECCAKEECE,
EEEGAGAGSEEE,
5 NNECACKCCNE,
EAAKEAAAK,
CCEAAAKDAAHC,
HCAAEEAAAKCH,
NGCGN(GPAGPP)₂NGCGN,
10 NGCGN(GAGAGA)NGCGN,
C(N)₃(GGAGVA)₆(N)₃C,
N₂(GAGAGA)(GPCGPP)(GAGAGA)N₂,
NGCGN(GSHGGS)(GAGAGA)N₅,
N₂H(GCAGAA)(GAAGAG)N₂,
15 N₂GCPGPP(GAAGPGAAG)GPPGPH(N)₃,
N₅GPCGHP GCPGPH(GPAGPP)(N)₅,
NGCGN(helical sequence)NGCGN,
NGCGN(helical sequence)H(helical sequence)N₅,
L₄H GC(helical sequence)L₅,
20 (GL)₅GC(helical sequence)H(GL)₅, and
(LV)₅GPCGHP GCPGPH(helical sequence)(LV)₅.
47. A film comprising the ordered biopolymeric material of claim 1 or 43.
48. A magnet, comprising the ordered biopolymeric material of claim 1 or 43, wherein the magnet is paramagnetic, aniferromagnetic, spinglass, superparamagnetic, ferromagnetic, ferrimagnetic, or antiferrimagnetic.
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49. A magnet comprising an ordered biopolymeric material of claim 1 or 43, wherein the magnet is pressure sensitive, and wherein the magnet is paramagnetic, aniferromagnetic, spinglass, superparamagnetic, ferromagnetic, ferrimagnetic, or antiferrimagnetic.